COMMENTS

Comment on "Quasielastic neutron scattering of two-dimensional water in a vermiculite clay" [J. Chem. Phys. 113, 2873 (2000)] and "A neutron spin-echo study of confined water" [J. Chem. Phys. 115, 11299 (2001)]

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In a pair of insightful papers,[1,2] Swenson *et al.* describe the dynamics of water in Na-vermiculite clay studied by time-of-flight[1] and spin-echo[2] neutron spectroscopy. In fitting the Q dependence of the quasielastic component that accounts for translational diffusion of water molecules, the authors utilize the expression for the full width at half maximum (FWHM) of the Lorentzian broadening previously used for the analysis of water dynamics in Ca^{2+}-exchanged montmorillonite[3]

$$\Delta E = \frac{2\hbar}{\tau}[1-\exp(-Q^2\langle r^2\rangle/2)], \tag{1}$$

where $\langle r^2\rangle$ is the mean square jump length and τ is an average residence time between two jumps. An exponential behavior of the Lorentzian broadening approaching the asymptotic value of $\Delta E = 2\hbar/\tau$ at high Q results from assuming a Gaussian distribution of diffusion jump lengths. However, the correct expression for the Q dependence of the Lorentzian broadening derived by Hall and Ross[4] is

$$\Delta E = \frac{2\hbar}{\tau}[1-\exp(-Q^2 r_0^2/2)], \tag{2}$$

where r_0^2 is the parameter of the normalized Gaussian distribution of jump lengths in three dimensions

$$\rho(\mathbf{r}) = \frac{1}{r_0^3\sqrt{(2\pi)^3}}\exp(-\mathbf{r}^2/2r_0^2) \tag{3}$$

corresponding to the normalized scalar distribution of jump lengths

$$\rho(r) = \frac{2r^2}{r_0^3\sqrt{2\pi}}\exp(-r^2/2r_0^2) \tag{4}$$

with mean square jump length $\langle r^2\rangle = 3r_0^2$. Therefore, using Eq. (1) instead of the correct expression (2) leads to underestimating the mean square jump length, as well as the diffusion coefficient $D=\langle r^2\rangle/6\tau$, by a factor of 3. At small Q, the expansion of Eq. (1) yields $\Delta E = 6\hbar DQ^2$, instead of the correct result $\Delta E = 2\hbar DQ^2$ as obtained from Eq. (2).

The properly estimated values of the translational diffusion parameters for water in a fully hydrated Na-vermiculite as should be obtained from fitting $\Delta E(Q)$ in Refs. 1 and 2 are listed in Table I. In fact, a simple analysis of the initial slope of the plots of FWHM as a function of Q^2 yields the correct diffusion coefficients three times larger than those reported by the authors of Refs. 1 and 2. For instance, from the FWHM of $\approx$200 μeV at $Q^2 \approx 0.5$ Å^{-2} in Fig. 3(c) of Ref. 1, the lowest Q point which the authors consider reliable, one can estimate a diffusion coefficient of about 30×10^{-10} m^2/s assuming a linear dependence $\Delta E = 2\hbar DQ^2$. Likewise, from the FWHM of $\approx$2 μeV at $Q^2 = 0.09$ Å^{-2} in Fig. 5 of Ref. 2, a diffusion coefficient of about 1.7×10^{-10} m^2/s can be estimated.

Interestingly, the values of the diffusion coefficients for water in Ca^{2+}-exchanged montmorillonite obtained in Ref. 3 appear to be consistent with their plots of FWHM as a function of Q^2, as if the authors used the correct expression (2) for the fitting despite reportedly using Eq. (1).

The properly estimated diffusion coefficient for slow water molecules[2] is still much lower than for bulk water, and does not affect the conclusions of Ref. 2 which are based on the fitted values of the relaxation time. The reevaluated values of the diffusion coefficient for fast water molecules[1] are more remarkable, being comparable to those of bulk water.[3,5] Previously reported values of the diffusion coefficient for water in confinement similar to that of bulk water include fully hydrated phycocyanin[6] and half hydrated Vycor glass.[7] In the data analysis, the authors of Ref. 1 use a Lorentzian

TABLE I. Reevaluation of the parameters for the translational motion of water in a fully hydrated Na-vermiculite obtained in Refs. 1 and 2.

	Residence time (ps)	Mean jump length $(\langle r^2\rangle)^{1/2}$ (Å)	Translational diffusion coefficient (m^2/s)
Fast component, $T=300$ K	2.3	1.9	26.4×10^{-10}
Fast component, $T=265$ K	16	4.0	16.5×10^{-10}
Slow component, $T=323$ K	126	3.6	1.7×10^{-10}

quasielastic broadening, which would result from a simple exponential relaxation function for the translational diffusion component. If this model, which has been originally used to describe the dynamics of bulk water,[5] is still applicable to water in confinement, then water confined in Na-vermiculite clay provides an interesting example of a high diffusion coefficient.

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